STUDY OF DECOMPOSITION BEHAVIOUR OF BINDERS AND THE EFFECT OF BINDER TYPE ON STRENGTH AND DENSITY OF ALUMINA SAMPLES

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By

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CERTIFICATE

This is certified that the work contained in the project entitled "STUDY OF DECOMPOSITION BEHAVIOUR OF BINDERS AND THE EFFECT OF BINDER TYPE ON STRENGTH AND DENSITY OF ALUMINA SAMPLES" by Shibani Das (Roll 107CR014) in partial fulfilment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

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Shibani Das

107CR014

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ABSTRACT

Organic binders are generally used during green shaping of ceramic bodies as these binders help in obtaining desired green density and defect minimization during pressing. The aim of the present study was two-fold. First was to study the decomposition behaviour of the three chosen binders (viz. PVA, Dextrin and Starch) through DSC/TG, FTIR and weight loss measurements in air. Second was incorporating these binders (in different amount) in reactive alumina (which was chosen as the base ceramic matrix) in different proportions. Subsequently these binder added powders were sintered in air at 1550°C and sintered pellets were characterized for apparent porosity, bulk density, strength and surface feature (through optical microscope).The strength and density measurements for both green and sintered samples were carried out and they showed varied trends. The green strength of starch added pellets was found to be least while PVA containing pellets had maximum green strength. In case of sintered pellets, starch added samples showed the most consistent set of strength values but its strength decreased with increase in binder concentration while the reverse occurred for PVA and dextrin containing pellets. Removal of binders is an important step during high temperature sintering process and under ideal conditions binder removal should be complete before consolidation of ceramic particles has started. When binder removal from sintered samples is incomplete, the sintered samples may contain defects such as black coring (due to incomplete burning of carbon which will be present as residual carbon below the surface), sealed pores, bloating, etc. Optical microscope imaging was done to observe the presence of such defects. These defects may lead to a variation in pore shape, size and distribution.

CHAPTER-1: INTRODUCTION

1.1 *Introduction*

Polymeric molecules and coagulated colloidal particles that are adsorbed and act as a bridge between ceramic particles provide a binding action. Some of these polymeric molecules also act as a deflocculant in a suitable environment. Many of these additives also provide several additional practical functions in ceramic processing such as formation of interconnected structures, gel-casting for formation of ceramic powders, processing of tapes for multilayer ceramic capacitor applications, etc. Usually a workable system is produced by using only one particular additive, but in some cases two or more types of additives having different molecular weights are also used. In ceramic processing these additives are referred to as binders although some of them may also be called flocculants. Binders may provide many functions in ceramic processing and thereby possess special names depending on their function. [1]

Depending on their functions the polymeric molecules or colloidal particles may be further subdivided as [1]:

(1) *Wetting Agent*: Their function is to improve the wetting behaviour of particles.

e.g. Water compatible acrylic levelling agent that is helpful in eliminating pinholes and craters is used as a wetting agent in non-toxic tape casting binder systems.

(2) *Thickener*: A thickener is used to increase the apparent viscosity of the processing system. e.g. an alkali-soluble, polyacrylate thickener is used as ceramic tile adhesive.

(3) *Suspension Aid*: A binder may help to reduce settling of particles in a suspension. e.g. microgels are used during processing of aqueous alumina.

(4) *Rheological Aid*: An appropriate binder type and concentration controls flow properties of a paste or slurry. e.g. different polymers are used in ceramic injection molding mixes.

(5) *Body Plasticizer*: A matrix of binder in a pressing powder, extrudate, or coating is used to provide plastic deformation behaviour to the system containing brittle particles. e.g. polyvinyl butyral resins are used during processing of green ceramic tapes.

(6) *Liquid Retention Agent:* It aids in reducing the liquid migration rate in a system. e.g. cellulose ethers are highly efficient water-retention agents in ceramic systems.

(7) *Consistency Aid:* This performs the task of altering the amount of liquid required in producing a particular type of flow. e.g. non-gel forming water soluble organic binders are used during injection molding of ceramic powders.

(8) *Binder:* The most important function of binder is to improve the as-formed product to provide strength for handling (green strength) before the product is densified by firing. In addition, a binder should possess one or more of the following characteristics:[2]

(a) Very low ash content.
(b) Easy burn-out character.
(c) Non-abrasive nature.
(d) Non-sticking property to the mould.
(e) Ease of dispersion.
(f) Non-toxic, inexpensive and environment-friendly.

Depending on the chemical nature, binders may also be classified as given in Table 1.1

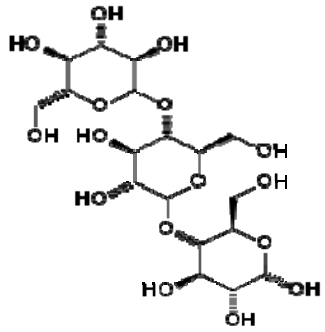
Table 1.1: CLASSIFICATION OF VARIOUS BINDERS ON THE BASIS OF THEIR CHEMICAL NATURE [1]

Particle type	Organic	Inorganic
Colloidal	Microcrystalline cellulose	Kaolin, Ball clay, Bentonite
Molecular	Natural gums: Xanthan gum, gum Arabic	Soluble silicates: Sodium silicate, Organic silicates, Ethyl Silicate
	Polysaccharides: Refined starch, dextrin	Soluble phosphates: Alkali phosphates
	Lignin extracts: Paper waste liquor	Soluble aluminates: Sodium aluminate
	Refined alginate: Na, NH_4 alginate	
	Cellulose ethers: Methyl cellulose, hydoxyethyl cellulose, sodium carboxymethyl cellulose	
	Polymerized alcohols: Polyvinyl alcohol	
	Polymerized butyral: Polyvinyl butyral	
	Acrylic resins: Polymethyl methacrylate	
	Glycols: Polyethylene glycol	
	Waxes: Paraffin, wax emulsions, microcrystalline wax	

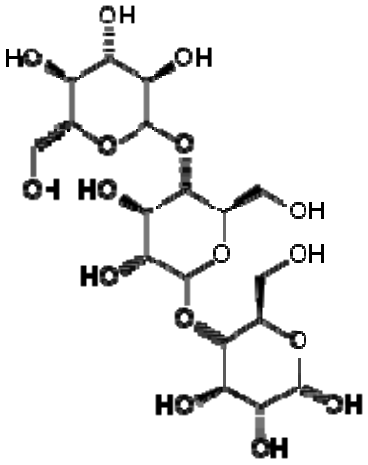
1.2 *Some of the major characteristics of three binders that are used in this study are as follows:*

PVA has a molecular formula $-[CH_2-\underset{\underset{OH}{|}}{CH}]-$ and is obtained by removal of acetate groups via partial or complete hydrolysis of polyvinyl acetate. PVA is a completely water soluble synthetic polymer and is fully degradable. Water acts as a plasticiser which reduces T_g of PVA and thus reduces its tensile strength, but increases its elongation and tear strength. The melting points of fully and partially hydrolysed PVA grades are 230°C and 180-190°C respectively. The boiling point of PVA is 228°C and it decomposes rapidly above 200°C as it can undergo pyrolysis at high temperatures. Dextrin is a low-molecular-weight carbohydrate produced by the hydrolysis of starch. [3]

The structure of dextrin is:



Dextrin has a molecular configuration that is less complex than that of starch and its chemical properties depend on the extent of the starch from which it is derived. Dextrin is water soluble but is precipitated by alcohol. Starch is a carbohydrate having molecular structure:



Starch is not soluble in cold water and decomposes very easily. [3]

CHAPTER-2:
LITERATURE REVIEW

2.1 ***Summary of literature:***

Baklouti et al. [4] studied the effect of PVA-W binder addition on the tensile strength of alumina. The results [Figure-2.1] show that addition of PVA-W binder increases tensile strength greater by a factor of 4 than the binder free alumina.

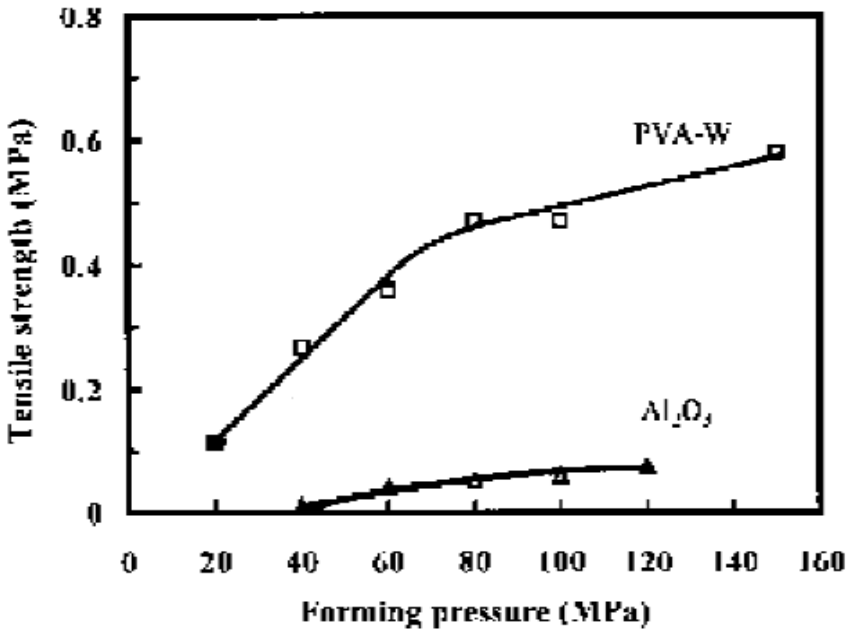


Figure-2.1: ***VARIATION OF STRENGTH OF SAMPLES PREPARED FROM PVA-W POWDERS AND FROM ORIGINAL ALUMINA POWDER WITHOUT ANY ADDITIVE VERSUS FORMING PRESSURE.*** **[4]**

The strength of compacts increases with forming pressure reaching a plateau at 100 MPa forming pressure. Mercury porosimeter experiments revealed that this pressure corresponded to the compaction stage where all intergranular porosity has been removed. [4]

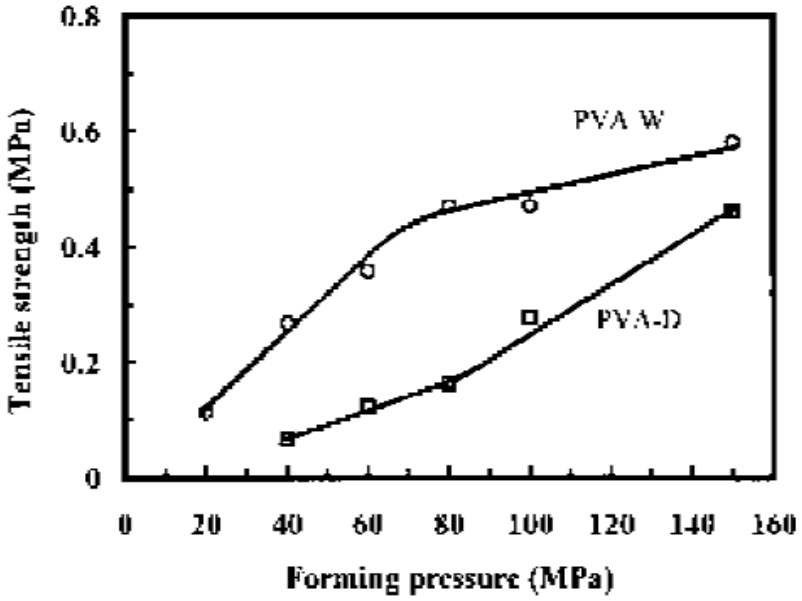


Figure-2.2: ***VARIATION OF SAMPLES PREPARED FROM PVA-W AND PVA-D POWDERS VERSUS FORMING PRESSURE.*** [4]

The same authors also studied that when two different binders were used (PVA-W and PVA-D), the strength was lower with PVA-D binder. The study led to the conclusions that binder type affects both density and mechanical strength. The strength of the pressed green samples results from an optimization between adhesive properties of polymeric shells that cover the granules and granule strength. When glass transition temperature of the binder is lower than the forming temperature, the interdiffusion between polymeric layers leads to strong bond formation between granules, but fracture propagation occurs through the granules due to the binder ductility. [4]

Tanaka et al. [5] studied the effect of granule on the microstructure of sintered compact.

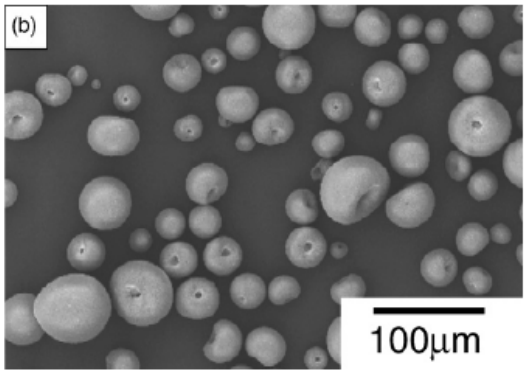


Figure-2.3: ***SCHEMATIC OF GRANULE CONTAINING PVA BINDER*** [5]

It was observed that for PVA addition non-uniform binder distribution was observed along with segregation at surface and sub-surface of alumina granules. Large intergranular interstices were also seen in addition to inhomogeneous internal structure of the compact. It was concluded that binder distribution affected strength and deformation behaviour of granules. [5]

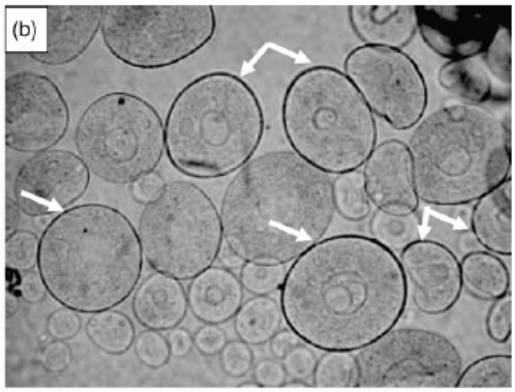


Figure-2.4: ***ALUMINA GRANULES CONTAINING PVA.*** [5]

Tanaka et al. [5] also observed that PVA is weakly absorbed on the particles and due to binder segregation; densification was hindered on absorption during pressing thereby forming a region of low compact density in the green body.

A number of studies [6-8] have been carried out to investigate the mechanisms of binder segregation in aqueous suspension of alumina-PVA suspensions during drying of alumina slurries with varying amounts of binder. The suspensions were dried in a beaker at different temperatures. A thermobalance was used to monitor the drying rates and to determine the binder distribution in axial direction the dried disc was sectioned. It was suggested that surface segregation resulted due to net effect of two processes, viz. liquid migration/evaporation and polymer back diffusion. These processes mainly depended on PVA concentration and drying temperatures.

TGA analysis approach is a systematic method for evaluating interaction between binders and slurry during drying. [9, 10] TGA analysis showed that slurry parameters such as solids loading, molecular weight, binder type and binder concentration significantly affected microstructural evolution and organic binder segregation of particulate suspensions during drying. The analysis also provided certain advantages such as less material and time requirement for studying binder drying characteristics. [10]

The thermal debinding and thermal degradation behaviour of alumina system with 3 wt% PVA was studied at high temperatures. It was observed that elimination of water which acts as a plasticizer took place at around 200°C. After the elimination of water, gradual decomposition of PVA took place between 200-600ºC via elimination of water and acetic acid followed by depolymerisation and oxidation of vinyl chains. The strength decreased with polymer weight loss. DSC and FTIR analysis showed that the polymeric binder removal was incomplete and a carbonaceous residue remained even after high temperature treatment. The strength values were low at 600°C due to binder removal. [11]

The increased demand for water soluble additives arose due to various drawbacks associated with organic binders and plasticizers. [12] During thermal debinding and evaporation of organic additives like alcohols, ketones, vinyl, polythene wax, etc, several safety and environmental shortcomings came up [13-15]. During heating of these organic binders, rapid gas generation during pyrolysis led to crack formation and shape deformation in partially sintered pieces. [16] Contamination of microstructures was caused by remaining carbonaceous residue. [12]

Studies have also shown that maltodextrin is an inexpensive binder which doesn't have the above mentioned drawbacks. [12] Water and CO_2 are the major decomposition products of maltodextrin and the volatile products are present in very low concentrations to cause any harm to the environment [12, 17] Schilling et al.[18] and other scientists have quoted many other advantages of maltodextrin some of which are mentioned below. [19,20]

(1) High powder-packing densities which minimizes shrinkage and warpage during drying, debinding, and sintering.
(2) High degree of plasticity during plastic molding and shape forming operations.
(3) Ability to produce strong, crack-free green bodies at very low concentrations thus promoting clean pyrolysis as well.

Although dextrins and maltodextrins are known to be made of D-glucose units, dextrins are branched polysaccharides whereas maltodextrins are linear ones having lower molecular weight fractions. The sorption phenomenon and interparticle electrostatic interactions in aqueous suspensions of ceramic powders due to their low pH value has made dextrin useful for aqueous processing of technical ceramics. [12]

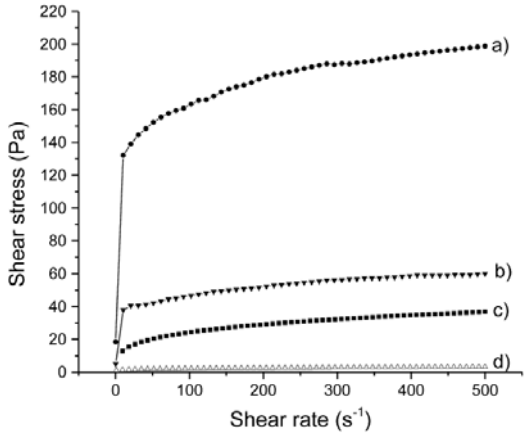


Figure-2.5: ***RHEOLOGY OF SUSPENSIONS CONTAINING 20 AND 30 VOL. % ALUMINA, WITH AND WITHOUT 0.9 KDA MALTODEXTRIN: (A) 30 VOL. % ALUMINA WITHOUT ADDITIVE; (B) 30 VOL. % ALUMINA WITH 0.64 WT. % OF 0.9 KDA MALTODEXTRIN; (C) 20 VOL. % ALUMINA WITHOUT ADDITIVE; (D) 20 VOL. % ALUMINA WITH 1.0 WT. % OF 0.9 KDA MALTODEXTRIN.*** [21]

Schilling et al. studied the rheology of alumina suspensions with maltodextrin (Fig 2.5). It was observed that the absence of polysaccharide additive provided a thixotropic behaviour of alumina suspensions. Addition of 0.64 wt. % 0.9 kDa maltodextrin drastically reduced shear stress at a given strain rate. Bingham-plastic like behaviour was exhibited by the specimens having higher concentrations of both water and polysaccharide. [21]

In another study, the effect of addition of low molecular weight maltodextrins on the rheological properties of alumina slurry was studied. It was found that although their low molecular weight aided in reducing the shear stress at a particular strain rate electrostatic interactions between the particles plays the most important role in reducing shear stress. [22]

Starch granules are insoluble in water below 50ºC, and therefore no major influence was observed on the granule structure while processing and handling at room temperature.

However when starch suspension was heated between 55-80ºC, weakening of intermolecular bonds between the granules took place leading to a fast and irreversible consumption of water and swelling of granules. [23]

When ceramic particles and starch were mixed to form a water suspension followed by pouring in a mould and heating to 60-80°C, swelling of starch particles was observed. This swelling enabled consolidation of ceramic particles by removal of water from the slip. This swelling also added strength and enabled demolding before drying. In addition it was also seen that when starch was used as a binder after binder burn-out and sintering took place, the porosity obtained in the body corresponded to the original amount, shape and size of the starch granules including the swelling that took place during consolidation. [24]

Starch has other advantages also such as easy burn-out nature, environment friendly and inexpensive. [25]

When starch was used as a binder, proper consolidation took place and even for high sample thickness (30-40 mm) compacts, the binder burnout and sintering proved to be a more time/energy efficient process for starch binder. In case of high starch containing bodies, cracks developed in the sintered body due to stresses generated during binder burn-out. [24]

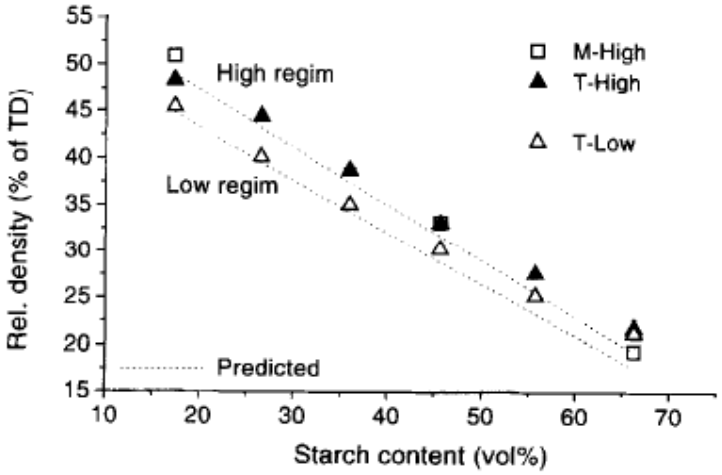


Figure-2.6: ***RELATIVE DENSITY OF CONSOLIDATED BODIES AFTER BURN-OUT AND PRE-SINTERING (1000°C) VERSUS CONTENT OF THE CHEMICALLY MODIFIED STARCHES.*** [24]

Figure 2.6 shows the variation of relative density of starch consolidated bodies after sintering at 1000°C. The graph shows that density decreases with increase in starch addition.

Predicted density considers any changes in dimensions after sintering.

In general density increased with decreased starch content but sometimes slight deviations have also been observed at higher starch content. [24]

2.2 ***Objective:***

The above discussions and different literatures reveal that during green forming/processing of ceramics, organic binders generally aid in achieving higher green density and in minimizing the process defects. This in turn can result in higher sintered density. However the density increase depends on binder type and amount. The aim of the present study is to investigate the decomposition behaviour of three different types of organic binder- PVA, dextrin and starch and to study the effect of binder type on the density and strength of sintered and green reactive alumina samples. The decomposition/burnout behaviour will be studied through DSC/TG and weight loss behaviour. FTIR studies will be undertaken to study the removal of different organic species during burnout.

This will be observed by heating the binder at different temperatures and studying the FTIR spectra. Densification behaviour will be studied through change in density from green pellet to sintered pellet. The sintered samples (with different types of binders) will be studied for strength measurement.

CHAPTER-3: EXPERIMENTAL DETAILS

3.1 ***Preparation of binder solutions***

The binders were used as aqueous solutions. The binder specifications are given below:

1) PVA was obtained from LOBA Chemie, chemical formula : $(C_2H_4O)_n$
2) Dextrin was obtained from LOBA Chemie, chemical formula : $(C_6H_{10}O_5)$ n x H_2O
3) Starch(soluble) was obtained from LOBA Chemie, chemical formula : $(C_6H_{10}O_6)_n$

The following tables give a flow chart of binder preparation steps for each type of binder.

Table3.1: ***PVA binder solution preparation***

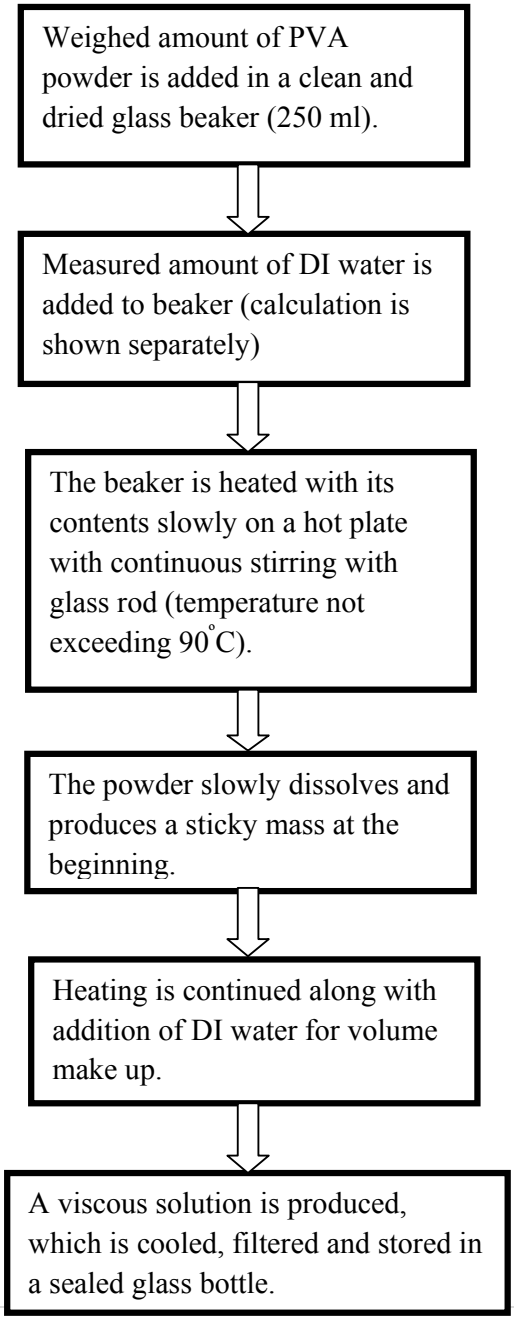


Table 3.2: ***Dextrin binder solution preparation***

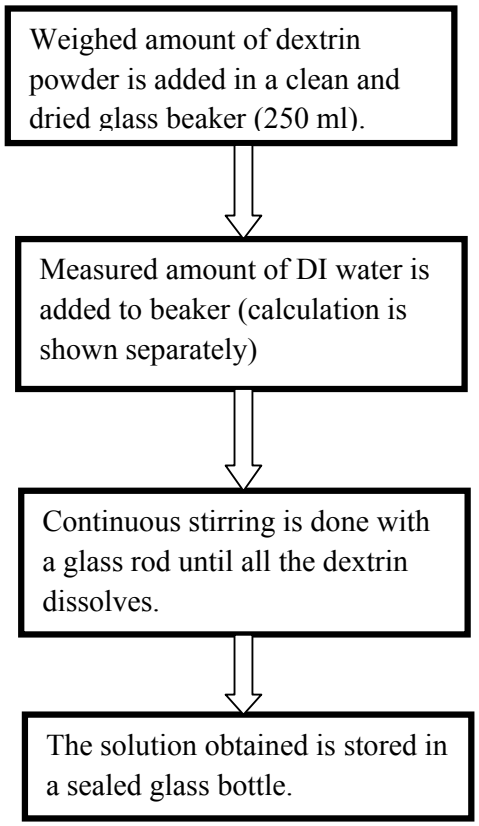
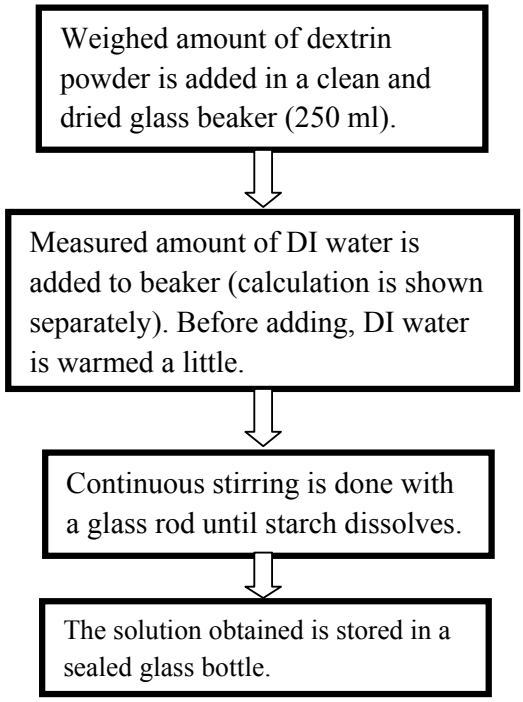


Table 3.3: ***Starch binder solution preparation***



Calculations: For making 2%, 3% and 4% solutions of each binder type 2gm, 3gm and 4gm binder powders respectively were used and volume of water used in each case was 100 ml.

3.2 ***Pellet making***

For making pellets 75μm fine reactive alumina powder was used. This reactive alumina was weighed and mixed thoroughly in an agate mortar pestle with each binder type and for each concentration. After mixing for 30 minutes, the paste was left in air to dry. After complete drying the hardened mass was finely ground. The dry ground powder was then measured to make the pellets.

Pellets were made by dry pressing under a load of 3.5 MPa, with a 25% pump speed and a dwell time of 60 seconds was given. A high carbon high chrome steel die of 12.5mm diameter was used. 3% Stearic acid solution was used for lubrication and acetone for cleaning the die to prevent contamination and sticking.

3.3 ***Sintering***

After pelletizing the samples were sintered in electrical resistance heating furnace (Prysalch & Co.) with $MoSi_2$ heating element at a temperature of 1550ºC for 2 hours along with an intermediate soaking period of 1 hour at 600ºC. The samples were heated at 3°C/min till 600°C followed by heating at 3°C/min till 1550°C.Following the holding at 1550°C, the furnace was switched off for cooling and the samples were taken after the furnace temperature reaches below 100°C.

3.4 ***DSC/TG***:

The DSC/ TG experiments were conducted in a Netzsch 449C Thermal Analyser. The samples were heated in flowing Ar gas atmosphere at a heating rate of 5ºC/min and 10ºC/min. The weight loss measurements were also done in the same instrument and the results are shown in Figures 4.1-4.6.

3.5 ***FTIR:***

The presence of different functional groups in the as prepared state as well as during different stages of binder burn-out was studied by Fourier Transform Infrared Spectroscopy, FTIR (Perkin Elmer US). The FTIR spectra were taken on the powder sample. The binders were pressed to a circular disc (10 mm Ø) by mixing small quantity of powder with KBr. The samples were scanned in the wave number range 4000-400 cm^{-1}.

3.6 ***Bulk density and apparent porosity measurements:***

To measure bulk density and apparent porosity of reactive alumina pellets, first the dry weight of pellets was measured. Then they were soaked in kerosene kept inside a beaker and were evacuated till all the air bubbles vanished. After that they were kept inside vacuum for few hours. After removing from vacuum the suspended weight and soaked weight of the samples were calculated. To obtain bulk density (B.D.) the following formula was used:

B.D. = (dry weight)*(0.79)/(soak weight-suspended weight)

To obtain apparent porosity (A.P.) in % the formula used is:

A.P. = (soak weight-dry weight)*100/(soak weight-suspended weight)

3.7 ***Compressive Strength measurement:***

The Biaxial Tensile Strength of the pellets were measured by breaking the samples in a Tinius Olsen Materials Testing Machine (HK10S model) was used. It has a maximum load cell capacity of 10 KN. The biaxial tensile strength, S was obtained using the formula:

$$S = (2*P)/ (\Pi*D*t)$$

where P → Maximum Load

D→ Diameter of the pellet

t→ Thickness of the pellet

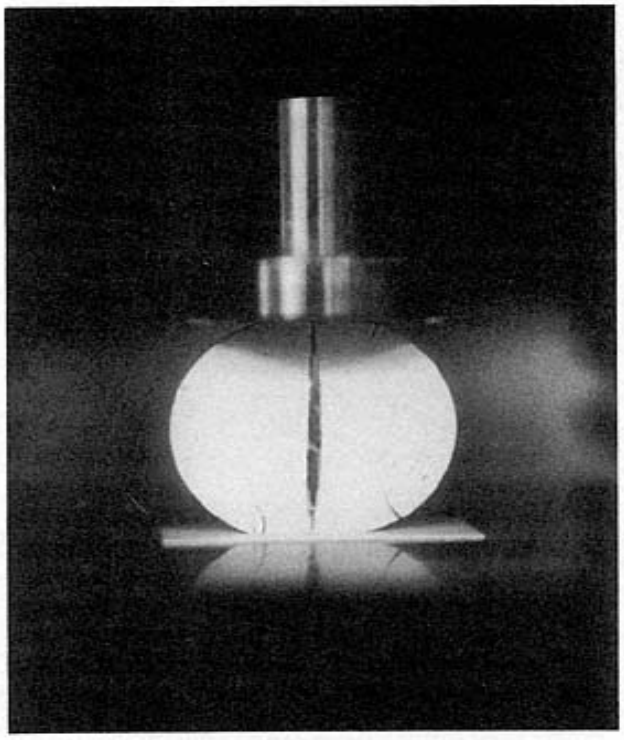


Figure3.1:*DIAMETRAL COMPRESSION TEST SHOWING LOADING AND FRACTURE MODE.* [1]

Bulk density, apparent porosity and compressive strength measurements were done for both green and sintered pellets.

3.8 ***Optical microscope Imaging:***

The selected sintered samples containing different binders were viewed in optical microscope. The images were taken using Olympus optical microscope fitted with a CCTV camera using Image analysis software. A magnification of 700X was used while procuring the images. The pellets were placed on a slide and then viewed through the monitor screen.

The lowest and highest binder containing samples for all the three binders (i.e. 2% and 4% binder addition) were chosen for optical imaging.

CHAPTER-4:
RESULTS
& DISCUSSIONS

4.1 ***DSC/TG GRAPHS:***

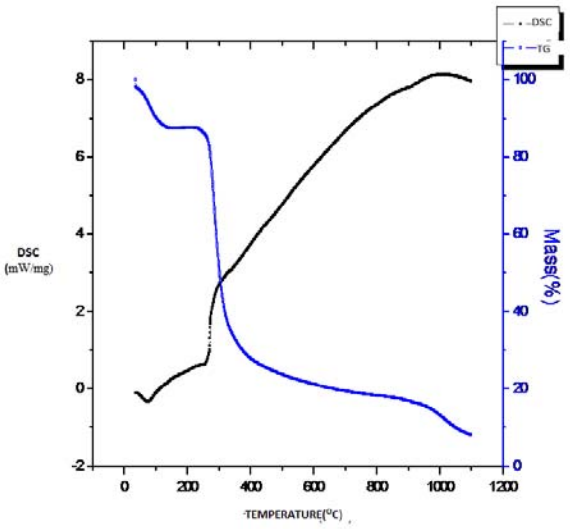


Figure- 4.1: ***DSC-TG GRAPH FOR DEXTRIN AT 5°C/MIN HEATING RATE***

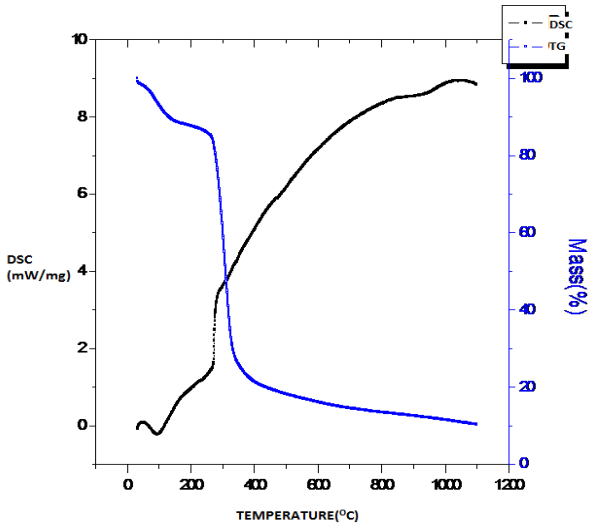


Figure-4.2: ***DSC-TG GRAPH FOR DEXTRIN AT 10°C/MIN HEATING RATE***

DSC/TG plot of dextrin at 5°C/min heating rate shows a broad endothermic peak at around 100ºC and another endothermic peak at 260°C. The TG curve shows weight losses over these two temperature ranges to be 40% and 60% respectively. No further major weight loss was observed beyond this temperature. It appears that these two peaks are due to removal of adsorbed moisture and decomposition of binder. TG curve of 5ºC/min heating rate shows that the approximate temperature at which there is maximum weight loss is 360°C.

For 10°C/min heating rate curve similar features to that of 5°C/min heating rate curve are observed.

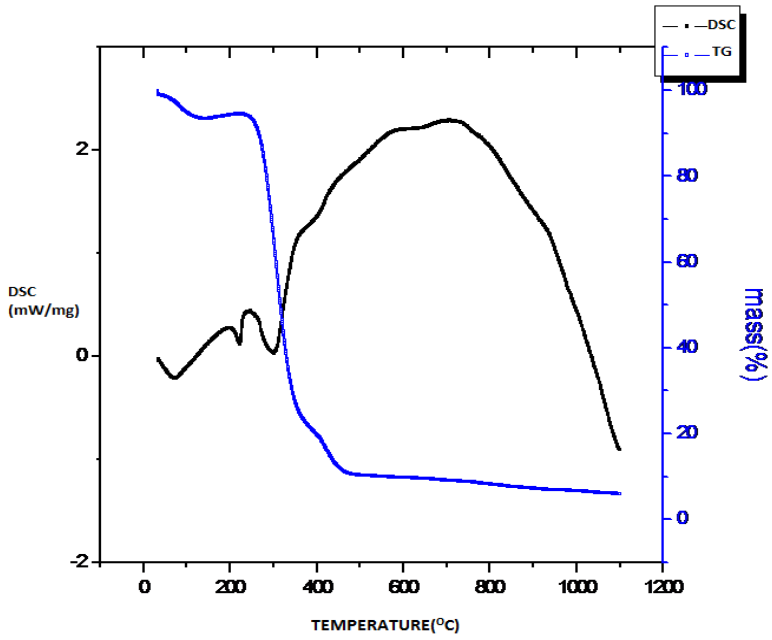


Figure-4.3: ***DSC-TG GRAPH FOR PVA AT 5 °C/MIN HEATING RATE***

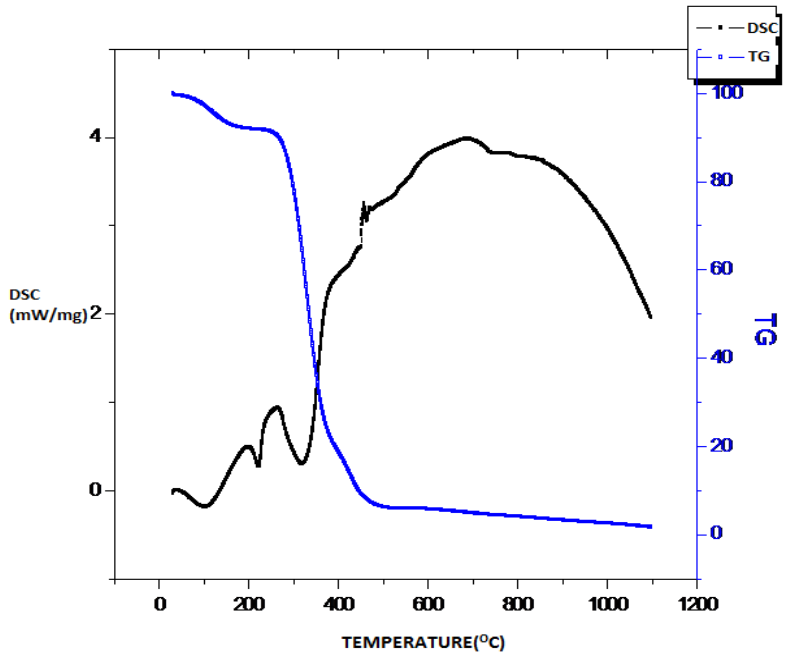


Figure-4.4: ***DSC-TG GRAPH FOR PVA AT 10 °C/MIN HEATING RATE***

Three very distinct endothermic peaks at around 100°C, 230°C and 260°C are observed for PVA. A broad exothermic peak is seen at around 740°C. The TG weight loss behaviour shows weight loss in three different stages matching with that of DSC. The peaks can be assigned to loss of hygroscopic moisture and breaking of high molecular weight organic species to a lower one. The exothermic peak corresponds to binder burnout. The maximum weight loss is around 90% of the original sample mass and takes place at around 400ºC

For 10°C /min heating rate curve, features same as that of 5°C/min heating rate curve are seen but peaks are less distinct due to faster heating.

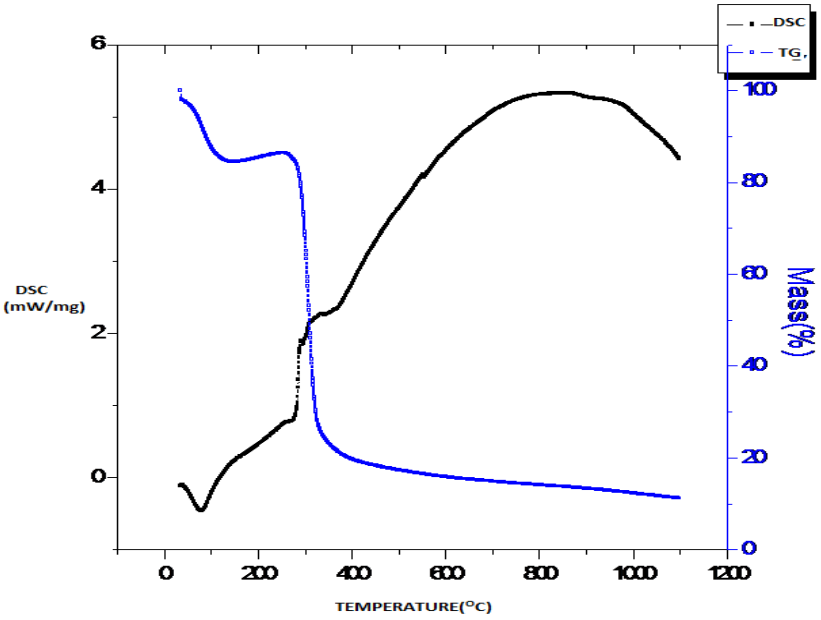


Figure-4.5: ***DSC-TG GRAPH FOR STARCH AT 5 °C/MIN HEATING RATE***

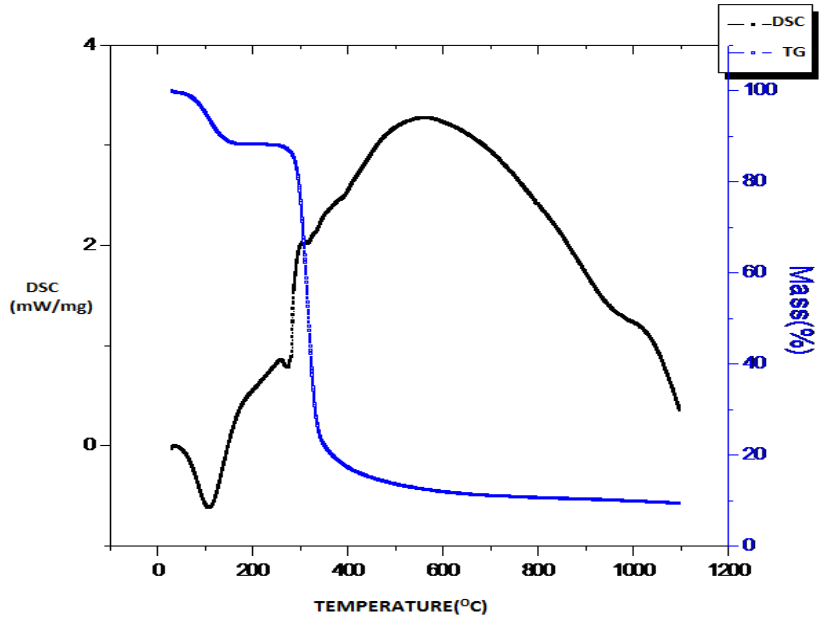


Figure-4.6: ***DSC-TG GRAPH FOR STARCH AT 10 °C/MIN HEATING RATE***

For starch distinct endothermic peaks at around 80°C, 280°C and 310°C are observed at 5°C/min heating rate. A broad exothermic peak is seen at around 880°C. Maximum weight loss takes place at around 380 °C and final residue remaining is 10% of the original mass. The weight loss behaviour corresponds to DSC curve at 80°C and 310°C. The weight loss is seen due to removal of moisture and decomposition of carbohydrates.

At 10°C/min heating rate curve similar to that of 5°C/min heating rate is seen but distinct peaks can no longer be seen.

4.2 ***FTIR Spectra:***

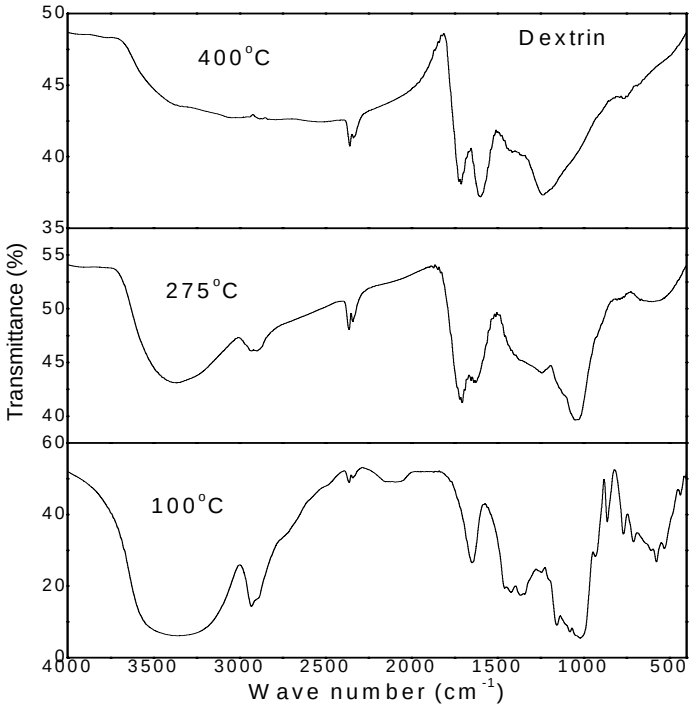


Figure- 4.7: ***FTIR SPECTRA FOR DEXTRIN***

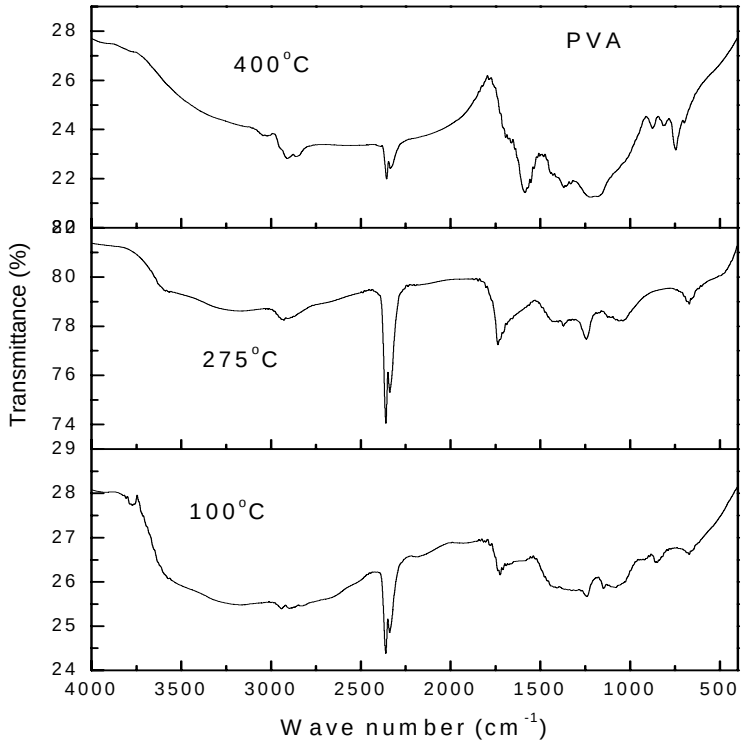


Figure 4.8: ***FTIR SPECTRA FOR PVA***

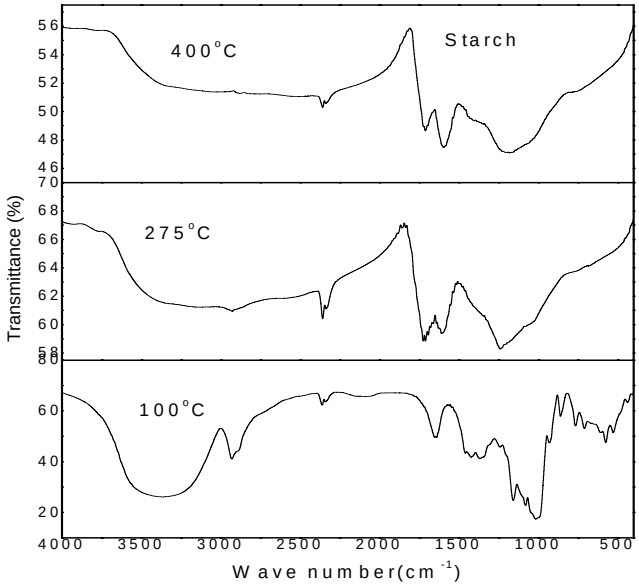


Figure 4.9: ***FTIR SPECTRA FOR STARCH***

Figures 4.7-4.9 show the FTIR spectra of Dextrin, PVA and Starch binders after it has been heated to three different temperatures, viz. 100°C, 275°C and 400°C. These three temperatures were selected on the DSC-TG pattern of the three binders (Figures 4.1, 4.3, 4.5) and it corresponds to the completion of different stages of decomposition.

At 100°C, all the three binders show a broad peak due to alcohols or water. The peak is of higher intensity for dextrin and starch which are basically starch derived binders and therefore contain excess of OH group. On the other hand, PVA shows a broad and not so distinct peak around 3500°C, probably indicated by bonded OH group. Besides, while dextrin and starch show a strong shoulder peak around 2934 cm^{-1}(due to aliphatic C-H bond stretching it is very small or negligible for PVA). On the other hand, the shoulder peak at 2360 cm^{-1} indicates C-O bonding due to CO_2 formation. The higher intensity of this peak in PVA (in comparison to starch and dextrin) may be because of two reasons:

(1) The breakdown of long chain polymers releasing CO_2 and/or CO.

(2) The lower amount of O-H stretching.

Carbonyl and aromatic peaks are observed between 1650-1570 cm^{-1} and these peaks are stronger in intensity in dextrin and in starch. The peaks in the range 660 cm^{-1} are indicative of solid residue. At 100°C, these peaks are of higher intensity and it decreases at higher temperatures (275°C and 400 °C). C-H carbonyl and aromatic peaks are present till 400°C which indicates that complete binder burn-out do not take place till 400°C. However C-O stretching (due to CO_2/CO formation) at 2360 cm^{-1}decreases but remains in PVA, but is very small for dextrin and starch. The spectra indicates that complete binder burnout doesn't take place till 400°C. [26]

4.3 *Weight loss measurements*

The DSC/ TG study of the three binders at 5°C/min showed that significant weight loss takes place only upto around 400°C and distinct weight loss is shown at temperatures around 100°C, 275°C and 400°C. Accordingly weight loss experiments were done on binder powders; they were dried at 100°C for 30 minutes, fired at 275°C for 30 minutes and fired at 400°C for 30 minutes. In all three cases, substantial amount of residue was obtained. The following table gives the residue obtained and the corresponding weight loss:

Table 4.1: ***WEIGHT LOSS BEHAVIOUR IN PVA***

Binder Type	Temperature (°C)	Initial binder weight(grams)	Weight after heating(grams)	%Weight loss
PVA	100°C	1.5018	1.4807	1.4
	275°C	1.5191	1.1415	24.86
	400°C	3.2823	0.6416	80.45

Table 4.2: ***WEIGHT LOSS BEHAVIOUR IN DEXTRIN***

Binder Type	Temperature (°C)	Initial binder weight(grams)	Weight after heating(grams)	% Weight loss
DEXTRIN	100°C	1.521	1.4908	2
	275°C	1.5088	0.9648	36.06
	400°C	2.9776	0.1018	96.58

Table 4.3: ***WEIGHT LOSS BEHAVIOUR IN STARCH***

Binder Type	Temperature ($^{\circ}$C)	Initial binder weight(grams)	Weight after heating(grams)	% Weight loss
STARCH	100°C	1.5516	1.4988	3.4
	275°C	1.5071	0.5032	66.61
	400°C	3.2171	0.1124	96.51

When heated to 700°C, it was observed that weight loss in case of PVA, Dextrin and Starch was 99.54%, 99.92% and 99.94% respectively.

At 400°C, since higher weight loss is observed for starch and dextrin over PVA therefore it may be concluded that starch and dextrin decompose fast while burn-out rate of PVA is minimum.

4.4 ***Bulk density, apparent porosity and diametral compressive strength measurements for green reactive alumina pellets containing binder***

Table 4.4: ***AVERAGE BULK DENSITY AND APPARENT POROSITY OF GREEN SAMPLES***

Binder type	**Concentration of binder (%)**	**Average Bulk Density(g/cc)**	**Average apparent porosity (%)**
PVA	2	2.66±0.10	31
	3	2.68±0.04	29
	4	2.64±0.05	29
Dextrin	2	2.58±0.02	36
	3	2.59±0.01	31
	4	2.60±0.02	31
Starch	2	2.75±0.12	33
	3	2.52±0.02	33
	4	2.5±0.05	30

Table 4.5: ***DIAMETRALCOMPRESSIVE STRENGTH OF GREEN REACTIVE ALUMINA PELLETS CONTAINING BINDER***

Binder TYPE	Concentration of binder (%)	Average Diametral Compressive Strength(MPa)
PVA	2	0.20±0.03
	3	0.43±0.06
	4	0.45±0.05
Dextrin	2	0.06±0.01
	3	0.08±0.01
	4	0.09±0.01
Starch	2	0.03±0.01
	3	0.05±0.01
	4	0.07±0.02

In green pellets the strength values lie in a comparable range with very less scattering in values. Green pellets with added starch binder had least strength. This may be due to least viscous reactive alumina paste formation with starch and it gave less binding action when there was no high temperature consolidation taking place.

4.5 ***Shrinkage, bulk density, apparent porosity and diametral compressive strength for sintered reactive alumina pellets with added binder.***

Table 4.6: ***AVERAGE VOLUME SHRINKAGE AND LINEAR SHRINKAGE OF SINTERED PELLETS***

Binder type	Concentration of binder (%)	Average volume shrinkage (%)	Average linear shrinkage (%)
PVA	2	13.52	4.89
	3	13.16	5.18
	4	13.89	5.09
DEXTRIN	2	12.12	4.55
	3	13.16	5.01
	4	13.3	5.34
STARCH	2	14.02	5.08
	3	13.19	4.61
	4	12.76	4.6

From Table 4.6 it is seen that average linear shrinkage and volume shrinkage values were comparable for all binder types and concentrations.

Table 4.7: ***AVERAGE BULK DENSITY AND APPARENT POROSITY OF SINTERED SAMPLES***

Binder type	Concentration of binder (%)	Average Bulk Density (g/cc)	Average apparent porosity (%)
PVA	2	3.01± 0.04	24
	3	2.99±0.03	25
	4	2.93± 0.03	26
Dextrin	2	3.00±0.02	24
	3	2.96± 0.01	25
	4	2.98± 0.02	25
Starch	2	2.90± 0.01	27
	3	2.84±0.03	28
	4	2.83±0.01	28

From Table 4.7 it can be seen that maximum porosity was observed in case of pellets containing starch binder which also had least bulk density values. Bulk density was higher for pellets containing PVA and dextrin.

Table 4.8: ***DIAMETRAL COMPRESSIVE STRENGTH OF SINTERED REACTIVE ALUMINA PELLETS WITH ADDED PVA***

PVA Concentration (%)	Diametral Compressive strength (MPa)	Average Strength (MPa)
2	15.89	20.93
	17.65	
	23.14	
	27.04	
3	16.31	24.26
	18.16	
	30.84	
	31.74	
4	23.17	26.31
	23.48	
	27.66	
	30.92	

Table 4.9: ***COMPRESSIVE STRENGTH OF SINTERED REACTIVE ALUMINA PELLETS WITH ADDED DEXTRIN***

Dextrin Concentration (%)	Diametral Compressive strength (MPa)	Average Strength (MPa)
2	3.98	12.56
	13.51	
	15.31	
	17.44	
3	4.09	20.58
	16.86	
	26.69	
	34.66	
4	16.75	23.04
	20.71	
	23.77	
	30.95	

Table 4.10: ***COMPRESSIVE STRENGTH OF SINTERED REACTIVE ALUMINA PELLETS WITH ADDED STARCH***

Starch Concentration (%)	Diametral Compressive strength (MPa)	Average Strength (MPa)
2	18.8	23.02
	22.75	
	23.56	
	26.99	
3	13.06	16.92
	16.16	
	16.64	
	17.82	
	20.9	
4	14	15.01
	14.24	
	15.9	
	15.91	

From Tables 4.8-4.10, it is seen that average strength values of PVA and dextrin containing pellets are increasing with increase in binder concentration. Although starch containing pellets display the reverse trend to that of one containing PVA and Dextrin, they have the most consistent set of strength values while most scattered values are seen for Dextrin binder. Also since starch containing pellets have a uniform set of strength values it appears that they have a homogeneous microstructure. As porosity was found to be higher for pellets with starch binder, it may be a reason for their lower strength values.

The scattered strength values of PVA and Dextrin added pellets might be due to incomplete binder removal at higher temperatures as sintering might have started at those temperatures.

Since black patches were observed after sintering in the pellets it is possible that due to incomplete binder removal some residual carbon was present. These black patches which may be due to black coring, sealed pores, etc might give variation in pore shape, size and distribution.

From Table 4.5 and Tables 4.8-4.10 it can be seen that green strength of pellets is very less as compared to that after sintering.

Thus average strength value cannot be the only parameter to judge the mechanical properties of a particular binder.

4.6 ***Optical microscope images and observations:***

The low magnification optical microscope image of sintered samples with different binder addition (PVA, Dextrin, and Starch) is shown in Fig (4.10-4.15).

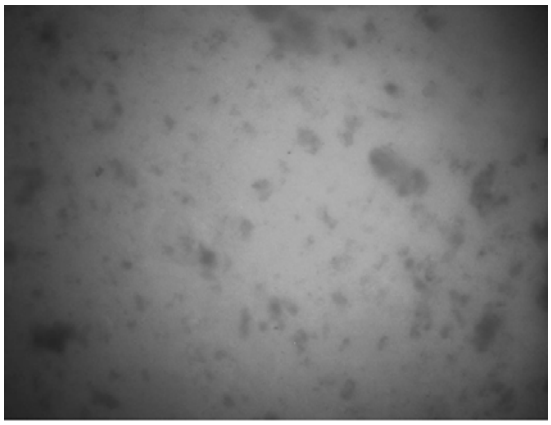


Figure 4.10: ***OPTICAL MICROSCOPE IMAGE OF SINTERED SAMPLE CONTAINING 2% DEXTRIN.***

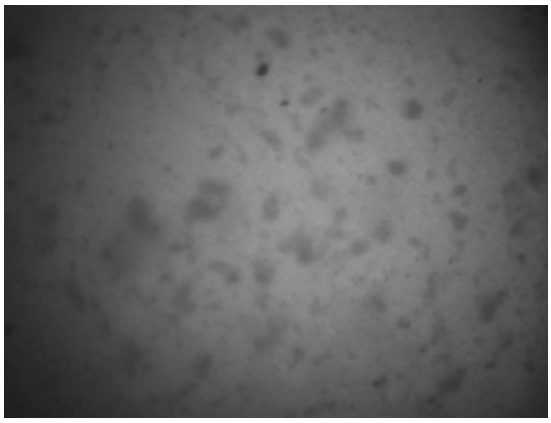


Figure 4.11: ***OPTICAL MICROSCOPE IMAGE OF SINTERED SAMPLE CONTAINING 4% DEXTRIN***

Fig (4.10, 4.11) shows the image of sintered samples with dextrin binder. Fig 4.10 is with 2% dextrin and Fig 4.11 is with 4% dextrin. The image clearly shows some dark spots (pores) and some surface patches (may be because of incomplete binder removal). The images don't show any major differences in appearance with increase in binder amount (2% and 4%). The density data for these two cases are very close also matches with this observation.

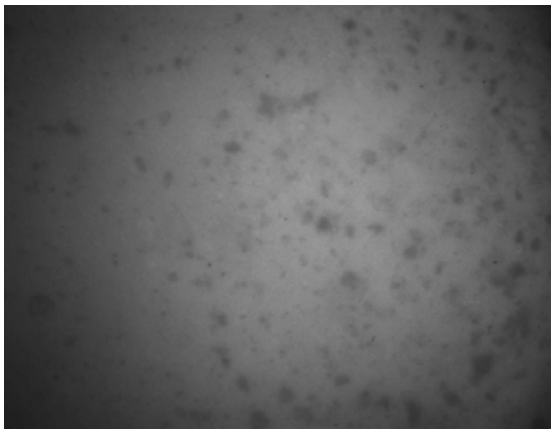


Figure 4.12: ***OPTICAL MICROSCOPE IMAGE OF SINTERED SAMPLE CONTAINING 2% PVA***

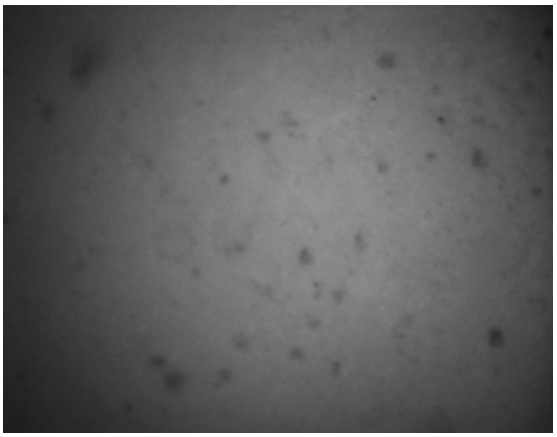


Figure 4.13: ***OPTICAL MICROSCOPE IMAGE OF SINTERED SAMPLE CONTAINING 4% PVA***

Fig (4.12, 4.13) shows the image of sintered samples with PVA binder. Fig 4.12 is with 2% PVA addition and Fig 4.13 is with 4% PVA addition. The sintered density data (2.9 and 3.03g/cc) also indicate similar behavior. The image with 4% PVA is virtually having very less patches.

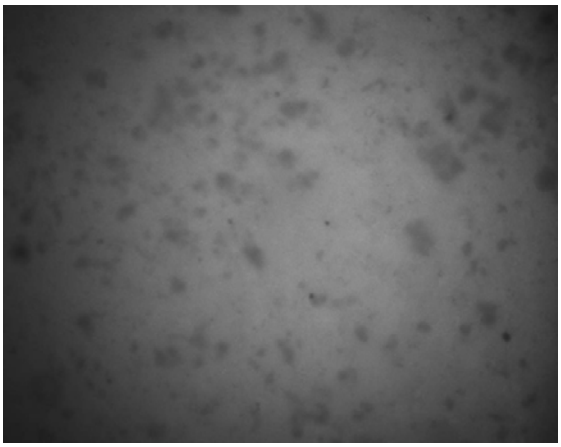


Figure 4.14: ***OPTICAL MICROSCOPE IMAGE OF SINTERED SAMPLE CONTAINING 2% STARCH***

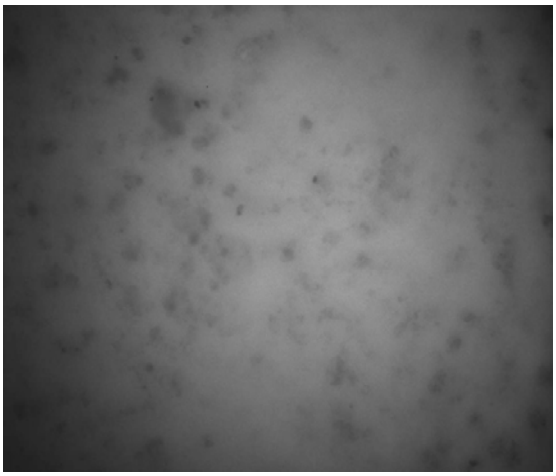


Figure 4.15: ***OPTICAL MICROSCOPE IMAGE OF SINTERED SAMPLE CONTAINING 4% STARCH***

Fig (4.14, 4.15) shows the image of sintered samples with starch binder. Fig 4.14 is with 2% starch addition and Fig 4.15 is with 4% starch addition. The images show residual pores in both cases which are nearly same fraction. Thus increase in starch addition does not affect the sintered density that much.

To summarize it can be said that PVA contributes to density increase while starch and dextrin don't contribute to density increase.

CHAPTER-5:

CONCLUSIONS

The significant observations that made are from the present study are as follows:

1) From TG curve maximum weight loss for PVA is observed around 400 $^{\circ}$C however decomposition of PVA continues even after 400°C as significant stretching/bending takes place even at this temperature (as seen from FTIR spectra) although for dextrin and starch minimum stretching/bending peaks are seen.
2) Starch added sintered pellets show a decrease in strength with increase in binder concentration whereas the trend is reverse for PVA and dextrin.
3) Starch added sintered pellets show a consistency in strength values whereas PVA and dextrin show scattered values which may be due to non-uniform pore size distribution.
4) Starch added green pellets have the least strength may be because of their higher apparent porosity.
5) When optical microscope images of sintered pellets were observed, black patches were seen on their surface which may be due to incomplete removal of binder below the surface of pellets.

CHAPTER-6:

SCOPE FOR FUTURE WORK

1) Larger sample size should be taken so that variation in values of binder concentration can lie in a greater range.
2) DSC/TG of green pellets should be carried out.
3) SEM study should be done.
4) Hg porosimetry should be carried out.

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